

# The underdoped-overdoped transition in $\text{YBa}_2\text{Cu}_3\text{O}_x$

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Oxygen doping in metallic  $\text{YBa}_2\text{Cu}_3\text{O}_x$  induces quadrupolar “ $\alpha$ -ortho”, and breathing “ $\beta$ -ortho” deformations of the  $\text{CuO}_2$  planes. Breathing  $\beta$ -ortho deformations favour hybridizations of the  $pd\sigma$   $\text{Cu}3d_{x^2-y^2}-\text{O}2p_{x,y}$  with the  $pd\pi$   $\text{Cu}3d_{x,z}, 3d_{y,z}-\text{O}2p_z$  bands relaxing the confinement of the carriers in the overdoped regime,  $x \geq 6.95$ .

## 1. INTRODUCTION

The overdoped regime of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  is accessible with heavy oxygen dopings close to  $x = 7$ . The crossover from the underdoped to the overdoped regimes occurs around  $x_{opt} = 6.92$ , nearly coinciding with a displacive structural phase transition [1]. It is suggesting to associate the structural instability close to optimum doping with a kind of barrier limiting  $T_c$ . The 123 bi-layer cuprates exhibit comparatively low “optimum”  $T_c$ ’s around 90 K, but chemical trends and pressure experiments imply that  $T_c$  is not yet at its optimum value. In this communication we discuss a mechanism being possibly responsible for the barrier limiting  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , and stabilizing the overdoped regime for  $x \geq 6.95$ .

## 2. DOPING INDUCED LATTICE EFFECTS

Oxygen doping of the parent cuprate  $\text{YBa}_2\text{Cu}_3\text{O}_6$  induces two displacive structural phase transitions: the first at the insulator metal transition around  $x = 6.42$  transforming the tetragonal unit cell of the antiferromagnetic insulator into the orthorhombic symmetry of the metal, and the second close to optimum doping,  $x = 6.95$ , changing the orthorhombic unit cell from the  $\alpha$ -ortho to the  $\beta$ -ortho type.

### 2.1. $\alpha$ -orthorhombic deformation

In the underdoped regime ( $6.42 \leq x \approx 6.86$ ) doping is well established to increase the orthorhombicity,  $2000(b - a)/(b + a)$ . Positive axial strain,  $\partial b/\partial x \geq 0$  expands weakly the  $b$ -axis, while negative axial strain,  $\partial a/\partial x \leq 0$  compresses strongly the

$a$ -axis, cf. Fig.1 (*left*). The opposite axial strains result in a *quadrupolar* instability in the orthorhombic basal plane, labelled  $\alpha$ -ortho.

### 2.2. $\beta$ -orthorhombic deformation

In the overdoped regime ( $6.95 \leq x \approx 7$ ) the  $b$ -axis strain changes its sign, hence doping shrinks both,  $a$  and  $b$ , resulting in a *breathing* instability of the orthorhombic basal plane, labelled  $\beta$ -ortho, cf. Fig.1 (*right*). Since both,  $b$ - and  $a$ -axis strains, are negative in all samples, independent on their various routes of chemical preparation, the planar breathing instability has to be considered as a generic property of the overdoped regime.

### 2.3. $c$ -axis stress

Doping compresses strongly the  $c$ -axis, usually described by a straight throughout all regimes up to  $x = 7$ . Samples synthesized in the absence of carbonate however were shown to exhibit a significant minimum in  $c(x)$  close to the onset of the overdoped regime [1]. Raman spectroscopy and Y-EXAFS confirm the  $c$ -axis anomaly also in other samples: the in-phase O2,O3 mode (out-of-plane) softens abruptly in the overdoped regime, while the static O2,3–Cu2 interlayer spacing (“dimple”) increases discontinuously by  $\approx 0.015 \text{ \AA}$  [2].

The strong contraction of  $c$  is nearly completely attributable to the compression of the Cu2–O1(Apex) bonds reflecting the charge transfer from the chains to the planes. The Cu2 atoms may be seen to be pulled out the  $\text{CuO}_2$  planes. Notably thereby the average Y–O2,3 interlayer spacings remain unaffected.

Doping across the underdoped–overdoped phase boundary continues compressing the Cu2–O1(Apex)

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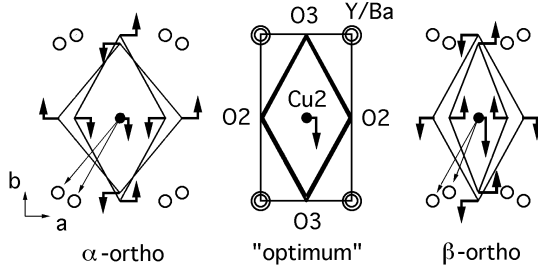


Figure 1. Incremental deformations of the copper-oxygen layers upon doping in the underdoped (*left*), optimum doped (*middle*), and overdoped regimes (*right*), viewed from the top, see text. Note that the “planes” are stacked layers, 0.25-0.29 Å thick. Cu2 is close to Ba–O1(Apex), and O2,O3 are close to Y–Y. The *a*-axis O2 are about 0.007 Å closer to Cu2 than the *b*-axis O3. The out-of-plane displacements are indicated by thick arrows. “Up” is towards the Y-layer, and “down” towards the Ba–O1 layer. The long arrows indicate the orthorhombic shear along (110).

bonds. In the overdoped regime however the average O2,3-layers experience a significant *repulsion* from the Cu2-layers, strongly contrasting with the underdoped regime. In some samples the Y–O2,3 inter-layer spacing remains nearly unaffected, and as a result  $c(x)$  develops a minimum [1].

### 3. CORRELATED DISPLACEMENTS IN THE $\text{CuO}_2$ PLANE

We have shown from Y-EXAFS that the Y–Cu2 bond lengths are almost independent on doping [2]. This suggests an “umbrella mode” to describe the static correlations between the Cu2 out-of-plane, and the O2, O3 in-plane displacements [3]. A refinement of the “umbrella mode” model may also explain the  $\alpha$ - and  $\beta$ -ortho deformations in the under- and overdoped regimes, respectively. The lengths of the rigid semicovalent in-plane copper-oxygen bonds can be safely assumed to be almost independent on doping, too. Then collapsing the “umbrella” moves the planar oxygens O2,3 out of their planes. As schematically shown in Fig.1 (*left*) the *quadrupolar*  $\alpha$ -ortho

instability pushes the O3 atoms beyond, and the O2 atoms beneath their planes. These shifts in opposite directions along *c* tend to cancel (depending slightly on the orthorhombicity), and the plane dimpling is solely determined by the Cu2 out-of-plane displacement. On the other hand side (Fig.1, *right*) the *breathing*  $\beta$ -ortho instability pushes both, O2 and O3 atoms, beyond their planes, thus increasing the dimpling not only by the Cu2 out-of-plane shift, but also by the oppositely directed O2,O3 out-of-plane shifts.

### 4. ELECTRONIC STRUCTURE EFFECTS

Out-of-plane displacements of the planar copper and oxygens were shown to have important effects on the electronic band structure near  $E_F$ . In particular they determine the strengths and symmetries of the interlayer hoppings [4]. Remote hybridization of the  $\sigma$  Cu4s orbitals with the  $\sigma$  Cu3 $d_{x^2-y^2}$ –O2 $p_{x,y}$  band provides interlayer hoppings with *d*-symmetry, exhibiting maxima at  $(\pi,0)$  and  $(0,\pi)$  in *k*-space. The strength of the *sdp* hybridization is mainly controlled by the length of Cu2–O1 (Apex) bond.

Hybridizations of the the  $pd\pi$  Cu3 $d_{x,z}$ –O2 $p_z$ , Cu3 $d_{y,z}$ –O2 $p_z$  with the  $pd\sigma$  Cu3 $d_{x^2-y^2}$ –O2 $p_{x,y}$  bands become feasible through Cu2 out-of-plane positions. Once activated,  $pd\pi$ – $pd\sigma$  hybridizations repel the O2,3 from the Cu2 plane [4].

We conclude, that the *quadrupolar*  $\alpha$ -ortho instability ought to suppress hybridizations of the  $pd\pi$  with the  $pd\sigma$  bands. The *breathing*  $\beta$ -ortho instability however ought to favour them and to provide a possible mechanism relaxing the confinement of the carriers, thus pushing the system into the overdoped regime.

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